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**NITROGEN TETROXIDE-STAINLESS STEEL
CRYOPANEL CORROSION AND COATING
DEGRADATION IN SPACE CHAMBER PROPULSION TESTING**

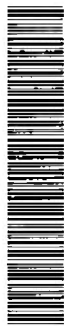
**P. G. Waldrep
ARO, Inc.**

April 1967

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**AEROSPACE ENVIRONMENTAL FACILITY
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FOREWORD

The research reported herein was sponsored by Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), Arnold Air Force Station, Tennessee, under Program Element 62405184, Project 5730, Task 573004.

The results of the research were obtained by ARO, Inc. (a subsidiary of Sverdrup & Parcel and Associates, Inc.), contract operator of AEDC, AFSC, under contract AF 40(600)-1200. The work was performed under ARO Project No. SW2607 from October 1965 to June 30, 1966, and the manuscript was submitted for publication on October 18, 1966.

All of the items compared in this report were commercial items that were not developed or manufactured to meet Government specifications, to withstand the tests to which they were subjected, or to operate as applied during this study. Any failure to meet the objectives of this study is no reflection on any of the commercial items discussed herein or on any manufacturer.

This technical report has been reviewed and is approved.

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ABSTRACT

Corrosion of cryopanel metals in space simulation chambers caused by contamination by fuels, oxidizers, or exhaust gases arising from propulsion systems testing may be a serious problem. Since data taken under operational conditions is needed, a preliminary study using nitrogen tetroxide and 300-series stainless steel was initiated. The temperature was cycled between ambient conditions and 77°K, and the pressure between 4 and 10^{-5} torr of oxidizer. A black epoxy film covered some of the samples. Welded stainless steel 304 sustained general corrosion with some pitting, and intergranular corrosion was detected in heat-sensitized weld areas. Epoxy coated stainless steel 304 samples demonstrated no apparent damage in one series of short tests, but pit formation in the coating, pitting beneath the coating, and intergranular corrosion in weld areas was detected in a longer test. Heat-treated and polished stainless steel 304-L pitted to an indeterminate depth. An epoxy coated sample of similar material suffered microscopic cracking and blistering of the coating and surface pitting beneath.

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SECTION I

INTRODUCTION

Propulsion systems testing in space simulation chambers may cause corrosion of the cryopanel material and other chamber components in varying degrees depending upon conditions of exposure. Some aspects of the corrosive nature of propellants and oxidizers have been reported (Ref. 1). However, the extent of corrosion should be estimated before actual space chamber operation to minimize serious corrosion problems. Since the space chamber environment is unique and different from conditions normally encountered, the lack of data on the effect of various variables on the rate of corrosion makes a study of these effects important.

Corrosion denotes the destructive attack of metal by chemical or electrochemical action with its environment. The harmful effects of corrosion may be either a total disintegration of the metal or damage to the microstructure in various possible ways to destroy the mechanical or other physical properties. General uniform corrosion with its resulting uniform disintegrating effect should be considered in the present experimental program. However, changes in the microstructure of the metal could be more important. Such changes include pitting, intergranular corrosion, and stress corrosion cracking. Thus, in the present report the microstructural damage is emphasized. Microscopic techniques using metallographic methods were employed. Corrosion deposit buildup was not sufficiently great to determine uniform corrosion. Degradation of organic coatings, plastics, and similar materials are not considered here as corrosion processes. In the present work, however, such degradation complicates and leads to corrosion problems.

Propellant or rocket engine exhaust product cryodeposits could cause slow cryopanel corrosion at low temperatures during extended periods of time. During warmup, the corrosion would be expected to be faster. The inevitable presence of water, even though the concentration may be quite small, is a complicating factor. An oxidizer such as fluorine with water present may form a more corrosive substance (like hydrogen fluoride, a powerful acid) and substantially increase the possibility of corrosion. Also, ultraviolet and infrared radiation from solar simulators and sunlight are other factors which may be important in affecting the corrosion rate since free radicals and highly reactive compounds may form under such conditions and interact with the adjacent surfaces (Ref. 2). Ultraviolet light is known to affect the rate of certain corrosion processes (Ref. 3). A study of ultraviolet and infrared radiation on

corrosion damage is not reported here, and such work is reserved for the future. The absence of an adequate protective film on the metal surface could result in very rapid and quite harmful corrosion. Film fracture caused by temperature cycling or other causes might result in corrosion even if a passivating film* had been formed initially. The possibility of film fracture necessitates temperature cycling in the experimental study of corrosion.

Migration of corrosion products from one metal surface to a different metal is another complicating factor. This possible effect could significantly affect the corrosion rate of the contaminated metal in a rather unpredictable way, especially in the presence of water or acid. Any contact of dissimilar metals within the chamber in the presence of water and a corrosive† could result in rather severe corrosion.

Normally a black organic coating is applied to the cryopanel surfaces facing the test object. Cat-a-lac® black, an epoxy coating, was used in the present study. These coatings, although usually chemically stable to moderate concentrations of various reactive substances, may undergo chemical degradation in the presence of highly reactive propellants, oxidizers, or exhaust products - especially with simultaneous exposure to ultraviolet and infrared radiation. Physical degradation such as cracking, blistering, or peeling from the metal surface is a distinct possibility under thermal cycling, ultraviolet and infrared irradiation, and exposure to contaminating substances. Especially harmful would be the possible buildup of corrosion products beneath the coating as a result of its permeability and resulting interaction of the metallic surface with the corrosive.

An experimental program to determine the corrosion effects on cryopanel materials such as stainless steel under temperature cycling from near 77°K to ambient conditions and pressures from 10^{-5} torr to several torr of nitrogen tetroxide (N_2O_4) was initiated. The materials were exposed to vacuum conditions with the corrosive as a cryodeposit at 77°K and to a corrosive pressure of a few torr at ambient temperature. The conditions were planned to approximate exposure conditions of cryopanel material under actual space chamber operation. The results of this research could prove quite useful in planning the construction and use of space simulation chambers.

*A passivating, or passive, film is a thin submicroscopic microcrystalline layer of compounds, usually mixed oxides containing water, which protects the underlying metal from corrosive agents.

†Corrosive agent, or the agent causing corrosion.

SECTION II

GENERAL CONSIDERATIONS

Corrosion problems with any metal are rather difficult to define over a wide range of conditions. In the case of space chamber operation, many different conditions which vary with time are to be expected. Leakage of propellant or oxidizer may occur by accident, and during long-term tests some leakage into the space simulation chamber will probably occur. With a condensable gas, a cryodeposit on the liquid nitrogen (LN₂) cryopanel will form. Upon warming the cryopanel an interaction between a reactive oxidizer, for example, and water would be expected. The degree of interaction would depend upon the amount of water and the amount of corrodent, together with the temperature, time, and physical state of the reactants. The product of this reaction could well be more corrosive than the original oxidizer, and under certain conditions accelerated corrosion might occur. Also, the hot exhaust gases from the rocket firings may raise the temperature of the cryopanel for a short time, to an indeterminate temperature, and reactions between the metal or organic coating and the contaminants could occur.

The various possible conditions should be investigated to determine the effects which occur. An estimate of the effect of each variable on the corrosion would prove invaluable in predicting damage under operational conditions. Many variables, however, are involved in such an analysis. These variables include temperature, time, concentration of corrodent, physical state of corrodent, concentration of water, ultraviolet and infrared radiation, concentration of corrosion products and other contaminating substances, state of passivity of the surfaces, previous history of the metal including exposure to other corrodents, and stresses in the metal. The rate of corrosion may vary with time, and a reasonable estimate of damage would then be dependent upon knowing this relationship.

Pitting is generally the prevalent form of corrosion in stainless steel as well as in other passive alloys and metals (Ref. 4), and this type of corrosion was detected in the present work. It should be noted that stainless steel may perform very well over a long period of time in many corrosive systems, but rapid penetration may occur in small areas resulting in pits (Ref. 4) to cause serious problems. Pits form more readily in a stainless steel which is metallurgically inhomogeneous (Ref. 5). Also, pitting may occur whenever a stainless steel is covered by an organic or inorganic film (Ref. 5) since any crevice, such as between two metal surfaces or between a metal and nonmetal, is a likely

place for pits to start. Polishing reduces the number of pits, but those which are formed tend to be larger (Ref. 4).

With the exception of the active pit bottom areas, the steel surface is passive. It is significant to note that under pitting conditions the metal may be damaged and eventually rendered useless even if a low overall corrosion rate exists (Ref. 6).

Surface passivating films on stainless steel are microcrystalline mixed oxides which contain considerable water (Ref. 7). Environmental conditions influencing the film properties control passivity effects and corrosion phenomena (Ref. 7). Minute defects may develop in the passivating film as a result of environmental factors. The passivating film may actually become thinner in a vacuum and presumably less effective. (See Ref. 8 on the growth of the film on polished samples and the behavior of the film thickness in a vacuum.) As a result, vacuum conditions could possibly alter the corrosion phenomena experienced by various metals in a significant manner so that passivity and resistance to corrosion are changed as compared with these properties under more usual conditions.

SECTION III EXPERIMENTAL PROCEDURES

3.1 APPARATUS

A stainless steel vacuum cell (Fig. 1) with a volume of approximately 136 liters, equipped with a mechanical pump and a Vac Ion[®] pump, was used as the test chamber. The chamber had a side flange attached through which the sample holder was inserted. Test specimens were arranged in such a way that the metal could be cooled to near LN₂ temperatures with either automatic flow or manual flow. In all but the first experiment, the interior of the cell was gold plated by vacuum deposition to minimize adsorption of water by the walls. Before gold plating, thorough cleaning was performed with acetone and then with 1, 1, 1-trichloroethane using sponges and precautions to avoid lint and dust contamination.

The initial sample of stainless steel consisted of a welded cryoliner and was constructed as shown in Fig. 2. A stainless steel enclosed thermocouple was fitted against the steel cryoliner by tension, and was shielded by a steel strip attached to the steel.

The next samples were in the form of two welded stainless steel cryoliners. Liquid nitrogen lines permitted flow of the coolant through the cryoliners. Stainless steel enclosed thermocouples were attached as in the case of the steel sample above.

The next series of samples was welded onto the same set of cryo-liners.

The heat-treated and polished stainless steel samples tested were placed on the steel cryoliners in the area of contact of the thermocouples by dismantling the thermocouples and supporting set screws by welded steel attachments. The temperatures of the samples were measured by attaching spring-loaded stainless steel enclosed thermocouples onto the samples.

The 300-series stainless steel samples were cleaned by means of an ultrasonic cleaner using 1, 1, 1-trichloroethane or by manually using acetone and then 1, 1, 1-trichloroethane. The polished samples were prepared by manual polishing using successively finer polishing paper with final polishing achieved by using an ultrasonic technique with fine alumina.

Emission spectroscopy was employed to identify and estimate the relative amount of silicon in the surface deposit of a preliminary run with stainless steel. The instrument used was a commercially available 3.4-m spectrograph

3.2 PROCEDURE

After the cell was pumped to about 10^{-5} torr, propellant grade nitrogen tetroxide (N_2O_4) was introduced into the cell from a stainless steel source outside the chamber. The pressure of the gas was measured with a 0- to 0.1-psid diaphragm-type pressure transducer calibrated against a reference pressure sensor. The transducer has a stainless steel diaphragm which is referenced by means of pumping on one side with a mechanical pump and has a precision of ± 0.03 torr. The readout of the transducer was recorded on a recorder with a precision of ± 0.02 torr. The cell was equipped with an ion gage and a thermocouple gage for reading cell pressures within their respective ranges. A sensitive pressure gage (Wallace and Tiernan gage with a precision of ± 0.02 torr) was also on the cell primarily as an alternate sensor to the transducer. The N_2O_4 was either condensed directly onto the sample surfaces or first onto a gold-plated cryosurface and then onto the sample surfaces after they were cooled to cryogenic temperatures. The temperatures of the metal specimens and the vapor were measured by means of copper-constantan thermocouples with readouts by means of a recorder. The thermocouples have a precision

of $\pm 3.3^\circ\text{K}$ in the 77°K range and the recorder has a precision of $\pm 1^\circ\text{K}$ in the 77°K range. The cell pressure was maintained between 10^{-5} and 10^{-3} torr by pumping with the Vac Ion pump to ensure that air or gaseous reaction products from the corrosion would not affect the test results by influencing the rate processes occurring on the metal samples.

The samples were raised to ambient temperature by discontinuing the flow of LN_2 and blowing N_2 gas through the lines. After the samples had been exposed over an extended time period and cycled between cryogenic and ambient temperatures, the N_2O_4 was pumped out of the cell by using a mechanical pump trapped with an LN_2 trap for collection of the N_2O_4 . Repeated flushing of the cell with N_2 gas and pumping removed the remaining corrodent.

The Cat-a-lac black epoxy organic coating was applied to the clean steel surfaces by either brushing or spraying after the metal surface had been degreased. Arc welding was used to join the steel where such samples were required.

The specimens were metallographically examined and Polaroid® micrographs made.

SECTION IV RESULTS AND DISCUSSION

4.1 PRELIMINARY RUN WITH STAINLESS STEEL

An initial corrosion test on stainless steel and Cat-a-lac black coated stainless steel in the presence of propellant grade N_2O_4 was performed in a chamber which had been cleaned by vapor blasting and which was equipped with a diffusion pump.

Figure 2 shows one side of the test specimens. The stainless steel specimen can be seen in the right background. Figure 3 shows the same side after exposure to 3 torr* of propellant grade N_2O_4 with three warmup periods of 5.8 hr to ambient temperature and cryogenic temperatures occurring

*Since the degree of dissociation of N_2O_4 into NO_2 is a function of temperature and pressure, these variables must be specified in order to calculate the ratio of gases present.

the rest of the time for a total exposure of about 24 hr. Table I lists the times and temperatures of exposure for the various samples. Figure 4 is a view of the Cat-a-lac black epoxy coated stainless steel surface with a deposit on the surface.

Analysis of the deposits by semiquantitative emission spectroscopy revealed that silicon was the major component. (See the apparatus section for the instrument used.) The silicon concentration was too large for an accurate estimate to be made of the amount present. The silicone diffusion pump oil used in the diffusion pump and the sand used to vapor blast the chamber were possible sources of this silicon contamination.

To eliminate both possible sources of silicon contamination, the diffusion pump was replaced with a Vac Ion pump, and the interior of the cell was gold plated. The gold plating of the cell minimized corrosive attack on the walls of the chamber. A mechanical pump with an LN₂ trap was used as a roughing pump. The presence of diffusion pump oil inside the chamber and especially on the test surfaces would have complicated the investigation, but it was relatively easy to eliminate this difficulty.

After these preliminary tests were concluded, a series of tests with 300-series stainless steel was run. Table I summarizes these results.

4.2 CORROSION OF WELDED STAINLESS STEEL WITH NITROGEN TETROXIDE

Stainless steel 304 welded with stainless steel 308 welding rod, with and without an epoxy coating, was tested in the presence of propellant grade N₂O₄. The exposure time was 214 hr and included five warmup cycles of 8 hr duration to ambient temperature, and the pressure of the N₂O₄ was 3.9 torr during the warmup cycle.

Figure 5 shows the specimens before the corrosion test. The Cat-a-lac black coated surfaces were obtained by brushing on the organic coating. A substantial coat was obtained; however, the thickness was not determined since suitable instrumentation was not obtained.

4.2.1 Uncoated Metal Samples

Figure 6 gives a view of the corroded stainless steel surface. The specks in the picture are areas of corrosion products. The amount of corrosion products present, however, was not sufficiently great for an analysis to be performed by means of emission spectroscopy.

Micrographs of cross-sectional areas of the test specimens were quite revealing. Figure 7 is a view of a cross section of the corroded stainless steel 304 and shows that general corrosive attack is present on the surface. However, because a reference surface cannot be estimated, the extent of the corrosion is not ascertainable. Figure 8 shows a cross section of the heat-sensitized area close to the welds. The grain boundaries display precipitated carbides together with delta ferrite.*

The beginning of intergranular corrosion** can be seen in Fig. 8. The depth of the corrosive penetration is not measurable, and longer duration runs would be needed to ascertain a rate. Since the degree of corrosion would need to be related to the conditions of exposure, a series of long-duration tests under specified conditions would be required.

Figure 9 displays heat sensitization† which occurs next to the weld and in part of the weld. Intergranular corrosion can be seen in the weld area, and susceptibility to this type of corrosion is clearly indicated. However, the depth of corrosion from the surface cannot be measured.

Figure 10 shows that pitting corrosion is occurring on the surface of the metal with a pit approximately 0.001 in. in depth. This pitting appears to be the result of the total dissolution of the grains along grain boundaries or of intergranular corrosion. A longer exposure time would be necessary to ascertain exactly the type of corrosion occurring.

*Delta ferrite is an allotropic modification of iron which forms around the austenitic grain boundaries in welded areas.

**Intergranular corrosion is a localized attack at the grain boundaries, resulting in loss of strength and durability (Ref. 5) and in some cases with loss of all recognizable properties of the metal (Ref. 4).

† Precipitation of carbides occurs when the stainless steel is heated in the sensitizing temperature range (from 750 to 1650°F) as the result of welding, causing susceptibility to intergranular corrosion (Ref. 5).

As a result of the above investigations, it would be advisable to minimize intergranular corrosion as much as possible.

Intergranular corrosion occurs in the heat-sensitized area around the weld. Stainless steel 304-L with a lower carbon (C) content would offer a more satisfactory intergranular corrosion resistance than stainless steel 304. Stainless steel 304 has a maximum of 0.08-percent C, whereas stainless steel 304-L has a maximum of only 0.03-percent C (Ref. 5). The higher carbon content of stainless steel 304 allows carbides to form along the grain boundaries in welding operations, making the sensitized areas susceptible to intergranular corrosion (Ref. 5). Although stainless steel 304-L also contains carbon, it should prove to be more resistant to intergranular corrosion when used with stainless steel 308-L welding rod than welded stainless steel 304 since stainless steels 304-L and 308-L contain less C than stainless steel 304.

4.2.2 Cat-a-lac Black Epoxy Coated Metal Samples

The results presented above for the uncoated stainless steel samples are compared here with the results obtained from similar samples coated with Cat-a-lac black epoxy.

Figure 11 is a view of the Cat-a-lac black organic coating which has a deposit of corrosion products. Corrosion products had apparently formed on both uncoated and coated samples. Two explanations may be advanced for similarity of the deposit on both types of surfaces. One explanation is the possible corrosion of the steel beneath the coating and migration of the products to the surface. The other explanation is a possible migration of corrosion product from the uncoated steel surfaces to the black coated surfaces. Further work would be necessary to determine the correct explanation.

Figure 12 shows the edge of the Cat-a-lac black and stainless steel interface and the structure of the metal with no corrosion indicated. In this instance the organic coating protected the steel from the corrosive action of N_2O_4 . In a later test a lightly painted steel surface, with the coating applied by spraying, showed evidence of pitting. Although the latter test was for a longer exposure time, the method of coating application and thickness may be quite important in providing optimum corrosion protection.

4.3 LONGER TIME CORROSION OF STAINLESS STEEL 304 WELDED WITH STAINLESS STEEL 304 AND 308

To compare the corrosion resistance of 304 and 308 welds on stainless steel 304, metal studs of stainless steel 304 were welded to the

steel cryoliners as shown in Fig. 13. Some of these were painted with Cat-a-lac black. The samples were exposed to 4.1 torr of propellant grade N_2O_4 in 20 warmup cycles to ambient temperature. (The time above $-150^\circ F$ was 55 hr.) During the remainder of the 720-hr exposure, N_2O_4 cryodeposit coated the samples.

4.3.1 Uncoated Metal Samples

General pitting corrosion is seen in Fig. 14, which is a cross section of stainless steel 304 welded with stainless steel 304 rod. No intergranular corrosion occurred since this is not in the sensitized welded area. The same type of pitting corrosion was found in stainless steel 304 welded with stainless steel 308 rod.

4.3.2 Cat-a-lac Black Epoxy Coated Metal Samples

A fairly severe carbide precipitation in one of the heat-sensitized areas of the Cat-a-lac black coated samples is shown in Fig. 15. Intergranular corrosion appears to have begun on the surface, but again the penetration could not be accurately ascertained. In welded areas of the other metal studs, since no carbide precipitation formed, no intergranular corrosion occurred.

Figures 16 and 17 are the micrographs of Cat-a-lac black coated stainless steel 304 welded with stainless steel 304 and 308, respectively. These two specimens experienced about the same degree of general pitting attack. The sample welded with stainless steel 308 rod displayed some pitting of the paint, thereby rendering the metal surface to be more susceptible to the corrodent. The corrosion may have been effected as a result of a possible inadequate formation of a passive film on the stainless steel coated with the paint. If this is the case, then the indication is that any defect such as a crack or pit in the paint would be a potential site for development of corrosion on the exposed metal surface. The unpassivated steel surfaces adjacent to the exposed metal would act as a large cathodic area with the exposed metal acting as the anode in the pitting process (Ref. 4).

Inability of the stainless steel to form a passivating film may account for the corrosion observed. Since passivating an entire space chamber is prohibitive in cost and time, a certain amount of corrosion will be inevitable unless the chamber naturally and adequately passivates itself under operational conditions. Even if natural passivation occurs, breaks in the film under temperature cycling with vacuum conditions will probably occur, thereby forming active sites for corrosion. One of the more important features of the environmental corrosion under space chamber

operational conditions is the uncertain maintenance of an adequate passivating film. Without such a film, corrosion will be facilitated.

4.4 PITTING CORROSION ON HEAT-TREATED POLISHED STAINLESS STEEL 304-L

Since welding of stainless steel 304-L, with its carbon content lower than that of stainless steel 304, results in decreased carbide precipitation along the grain boundaries of the steel, stainless steel 304-L is considered to be less susceptible to intergranular corrosion than stainless steel 304 (Ref. 5). However, welded stainless steel 304-L is not immune to intergranular corrosion. Austenitic stainless steels are sensitized to intergranular corrosion in the temperature range from 750 to 1650°F (Ref. 5) which occurs during the welding operation. Samples of the stainless steel 304-L were heat treated for one-half hour at 1075°F and then polished to a mirror finish to facilitate the definition of any tiny pits which might subsequently form on the surface as the result of corrosion.

Samples of the polished steel and Cat-a-lac black coated polished steel were exposed to N_2O_4 at a pressure of 4.0 torr during the warm-up cycles. The samples were maintained at a temperature above -150°F for 448 hr and at a temperature below -150°F for 414 hr. There were seven cooldown periods during which the corrodent was a cryodeposit on the samples.

Microscopic examination of the uncoated samples revealed surface pitting, Figs. 18 and 19. The pitting depth was indeterminate since the available instrumentation could not measure such small depths. The Cat-a-lac black coated surface indicated cracking and blistering of the protective coating with what appeared to be pitted metal exposed at some of the defects in the paint, Fig. 20.

The pitting was the result of the action of a corrodent at certain discrete spots on the surface of the metal. There was no microscopic or other evidence of a general attack - that is, corrosion occurring uniformly over the entire surface - on any of the polished samples examined. In fact, the polished surfaces retained a bright luster.

SECTION V SUMMARY OF RESULTS AND CONCLUSIONS

In a series of vacuum chamber corrosion tests, stainless steel 304 welded with 300-series stainless steel rod was found to undergo general corrosion, pitting, and, in heat-sensitized areas, intergranular corrosion. Cat-a-lac black epoxy films did not protect the underlying metal from corrosion, except in a brief exposure. The epoxy coating in one test had observable blisters and cracks. Heat-treated and polished stainless steel 304-L with and without the epoxy coating exhibited shallow pit formation on the surface.

The conditions of each test and the results are presented in Table I.

It is recommended that a stabilized stainless steel, such as stainless steel 304-L, be used for cryopanel construction to minimize intergranular corrosion. A comparable quality welding rod, such as stainless steel 308 ELC, should be used for the same reason.

The rate of corrosion was not established in these tests. Further work is required for determination of definite corrosion rates. It is suggested that a series of longer duration tests be established for rate measurement studies. In addition to welded stainless steel, stressed samples could be tested simultaneously to check for stress corrosion cracking. Since copper and aluminum may be used for cryopanels, these materials could be tested. Welds, brazes, and organic coatings with these materials should be examined. Contact of dissimilar metals could lead to galvanic corrosion. This possibility should be investigated. The effects of important variables such as concentration of corrodent and water, temperature, time and electromagnetic irradiation might be studied. Other corrodents - fuels, oxidizers, and rocket exhaust products - could be studied in a similar manner.

To determine accurately the corrosion damage, a number of different metallographic and chemical techniques should be employed. These methods include weight changes, corrosion product analysis, pit depth and number measurements, intergranular and stress corrosion cracking penetration measurements, degradation effects on the organic or other coatings, gas analysis of corrosion product gases and corrodents, and possibly other methods such as electrochemical measurements within the vacuum environment.

Accurately determined corrosion effects under specified conditions should enable design and operating personnel to minimize damage to space chamber components in propulsion systems testing.

REFERENCES

1. Boyd, W. K., Berry, W. E., and White, E. L. "Compatibility of Materials with Rocket Propellants and Oxidizers." DMIC Memorandum 201, January 29, 1965.
2. Rowe, L. C. "Effect of Sunlight on the Corrosion of Steel." Corrosion, Vol. 17, No. 6, 1961, pp. 93-94.
3. Bass, A. M., Broida, H. P., eds. Stabilization of Free Radicals at Low Temperature, U. S. Bureau of Standards Monograph 12, Government Printing Office (1960).
4. Uhlig, H. H., ed. The Corrosion Handbook. John Wiley & Sons, Inc., 1948.
5. Uhlig, H. H. Corrosion and Corrosion Control. John Wiley & Sons, Inc., 1963.
6. Schwenk, W. "Theory of Stainless Steel Pitting." Corrosion, Vol. 20, No. 4, 1964, pp. 129t-137t.
7. Nielsen, N. A. "Passivation of Stainless Steel." Symposium on Corrosion Fundamentals, A. de S. Brasunas and E. E. Stansbury, eds., University of Tennessee Press, 1956, pp. 148-169.
8. Andreeva, V. V. "Behavior and Nature of Thin Oxide Films on Some Metals in Gaseous Media and in Electrolyte Solutions." Corrosion, Vol. 20, No. 2, 1964, pp. 35t-46t.

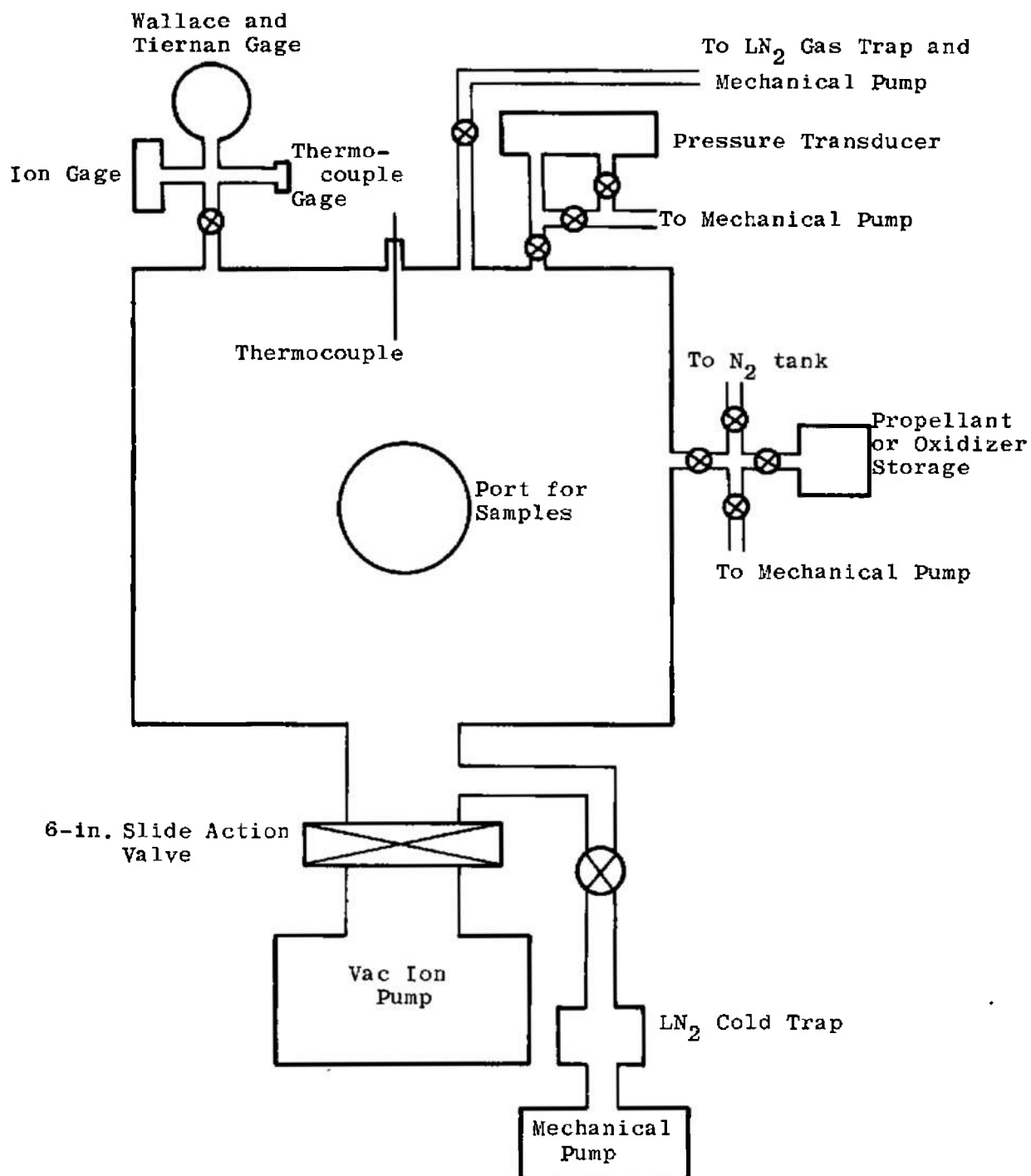


Fig. 1 Simplified Diagram of Test Chamber Arrangement

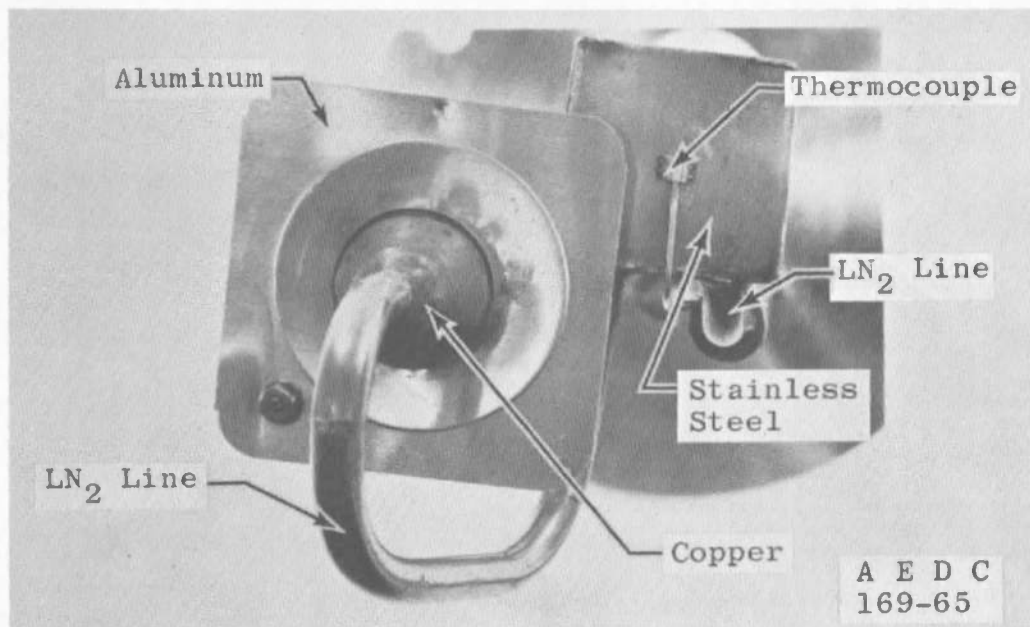


Fig. 2 General View of Stainless Steel Test Sample before Test

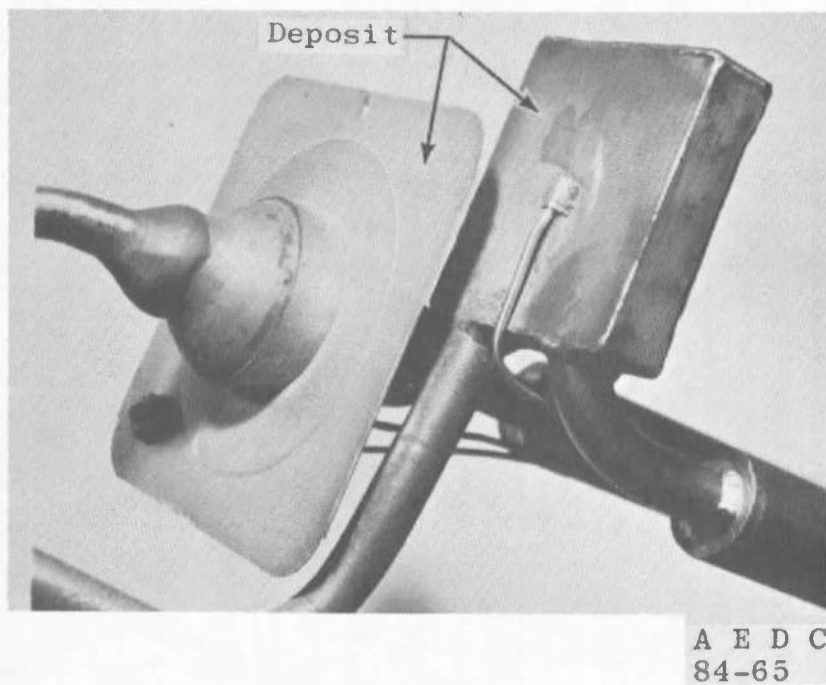
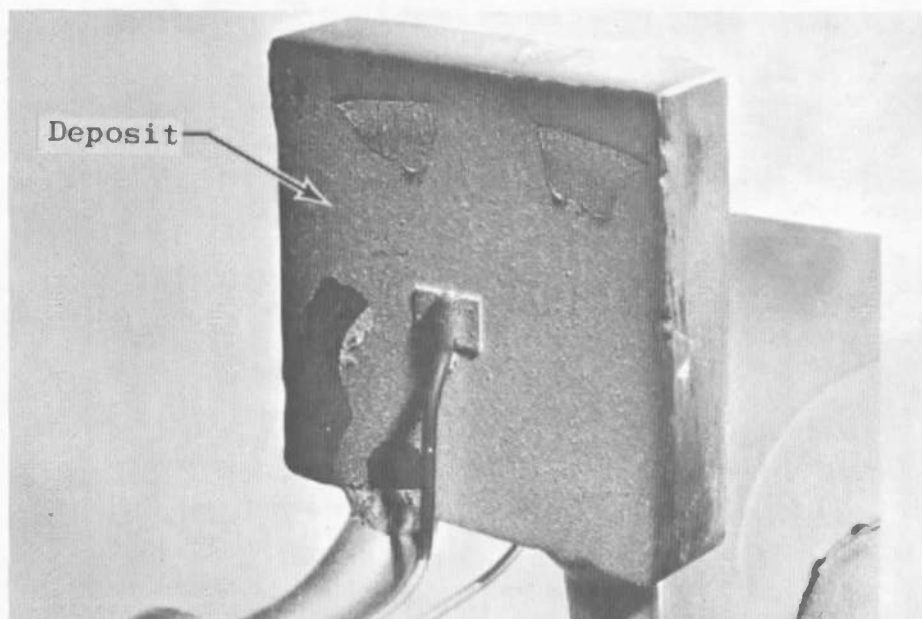
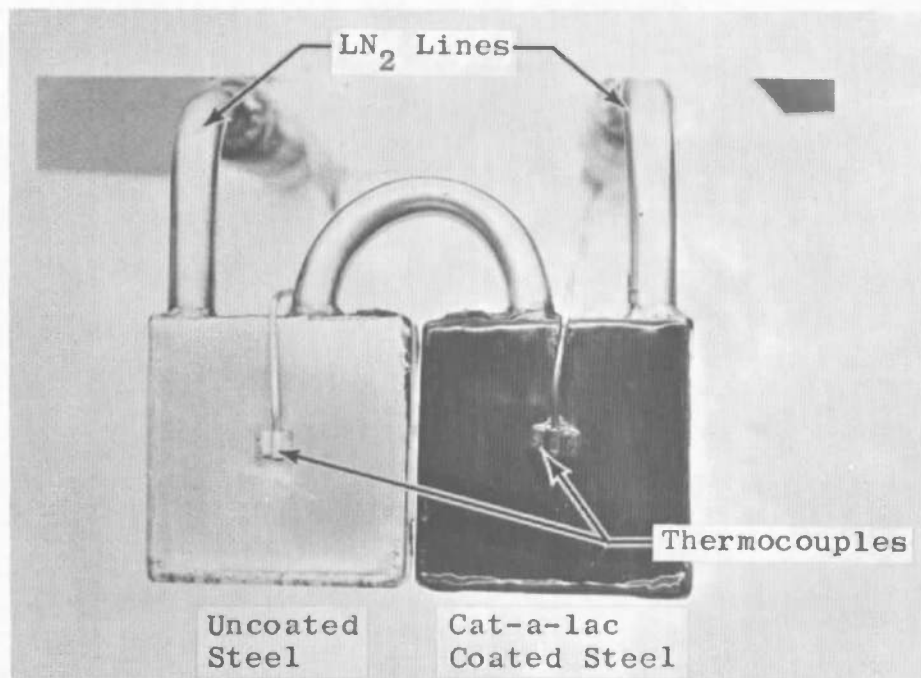


Fig. 3 Corroded and Contaminated Stainless Steel Sample after 24-hr Exposure to Nitrogen Tetroxide Cycling



A E D C
82-65

Fig. 4 Contaminated Cat-a-lac Black Coated Stainless Steel Sample after Test



A E D C
1232-65

Fig. 5 General View of Stainless Steel and Cat-a-lac Black Coated Stainless Steel before Test

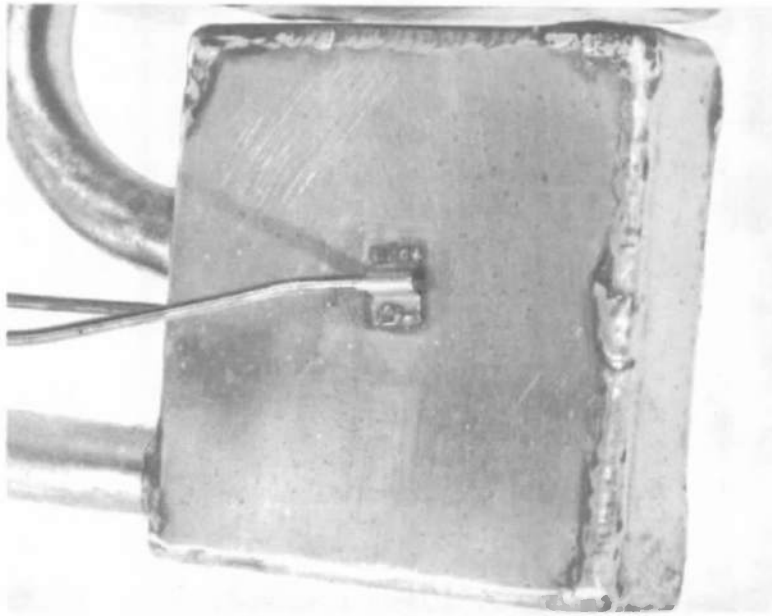
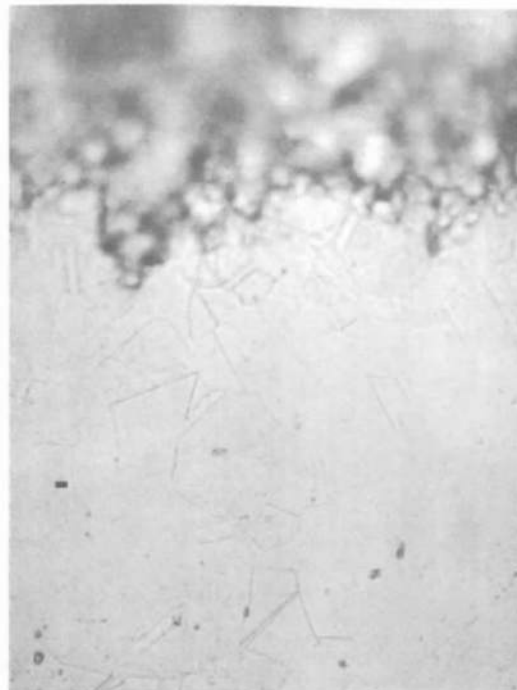


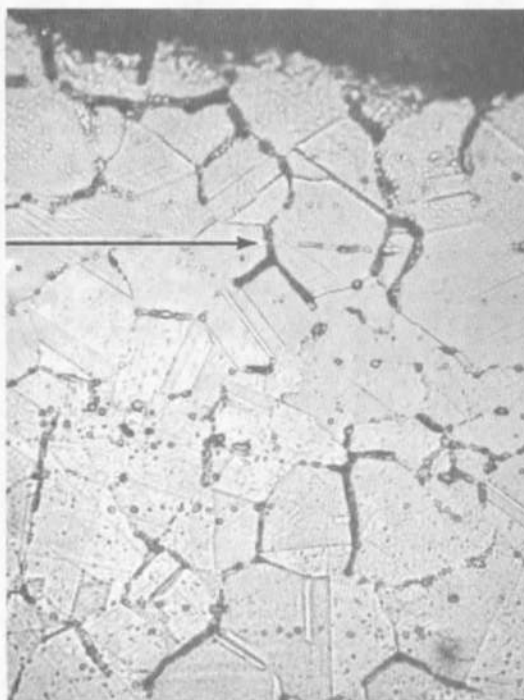
Fig. 6 Corroded Stainless Steel after over 200-hr Exposure to Nitrogen Tetroxide Cycling



500X ETCHANT-OXALIC ELECTROLYTIC

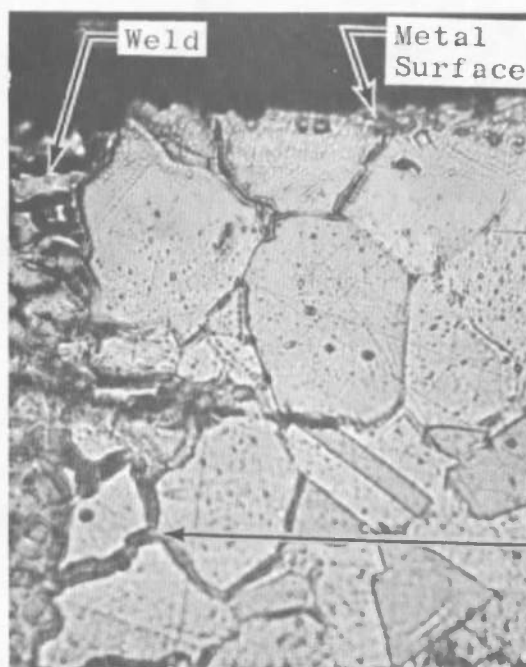
Fig. 7 Micrograph of Cross Section of Stainless Steel 304 Showing Corrosion

Carbides
along
Grain
Boundaries



500X ETCHANT-OXALIC ELECTROLYTIC

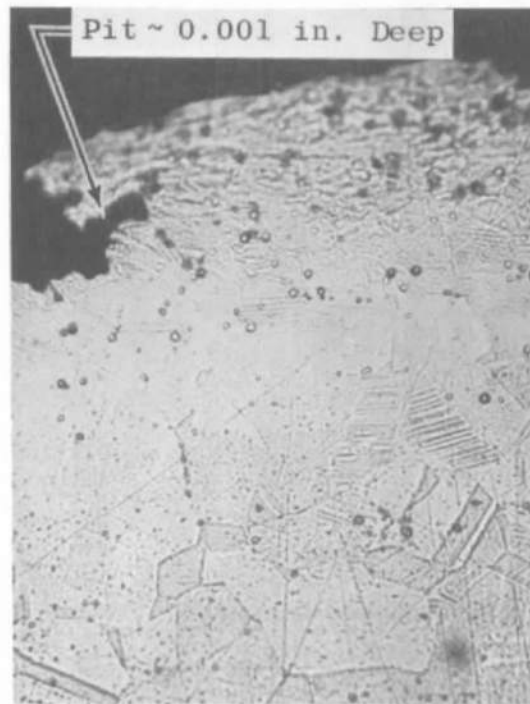
Fig. 8 Micrograph of Cross Section of Sensitized Stainless Steel 304 near the Welds



Carbides
along
Grain
Boundaries

500X ETCHANT-OXALIC ELECTROLYTIC

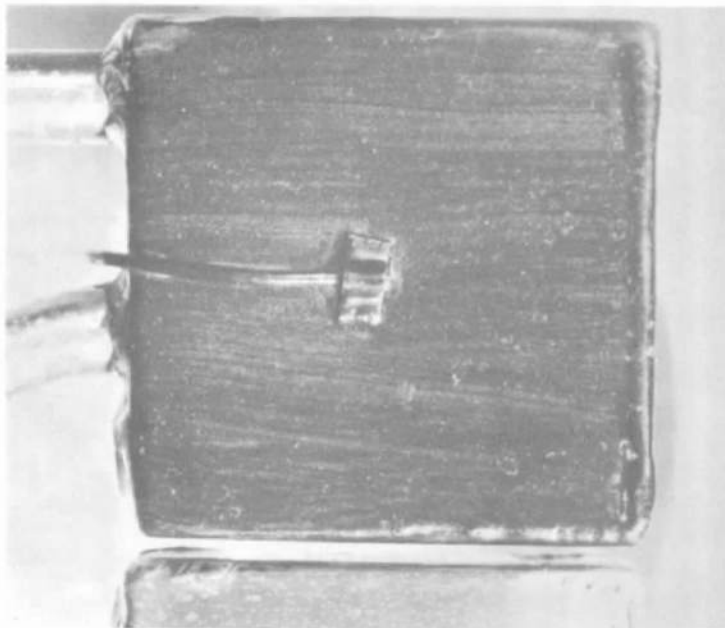
Fig. 9 Micrograph of Cross Section of Sensitized Stainless Steel 304 Weld Area



Pit ~ 0.001 in. Deep

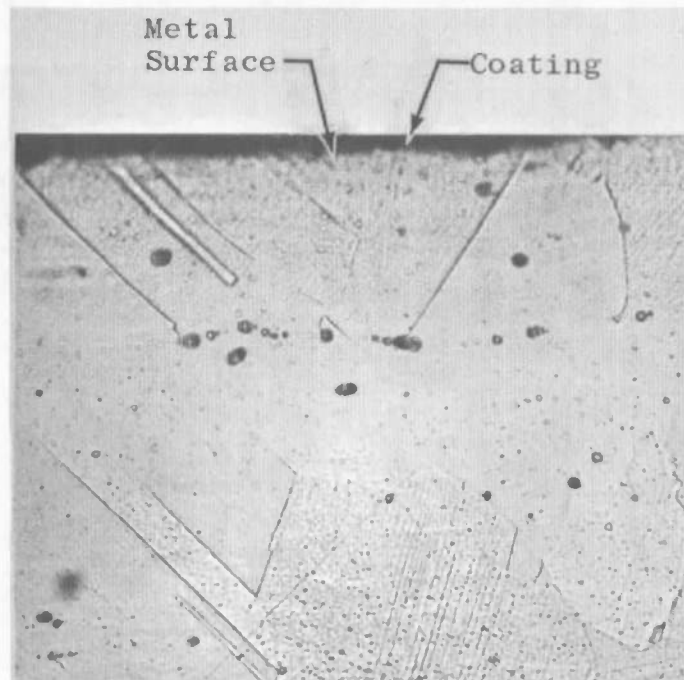
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Fig. 10 Micrograph of Cross Section of Corroded
Stainless Steel 304 Showing Pitting



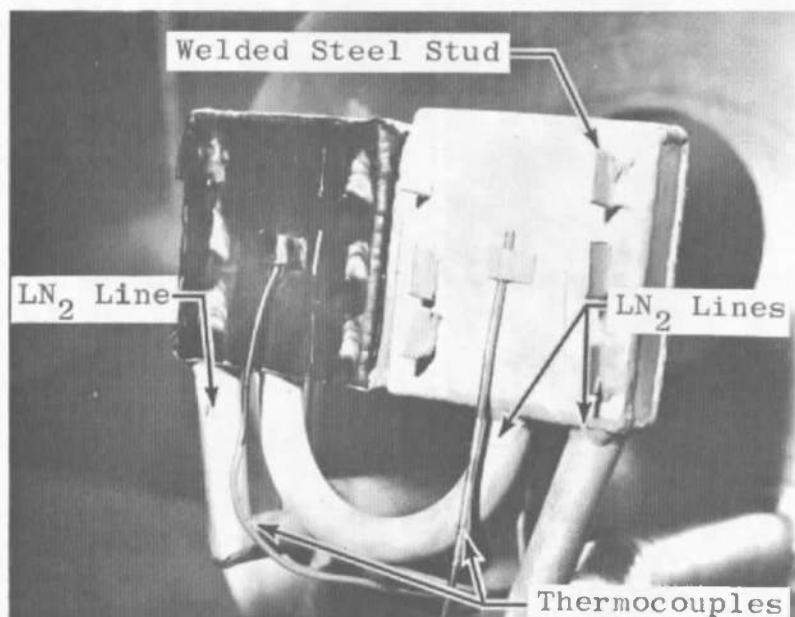
A E D C
1916-65

Fig. 11 Corrosion Product Contaminated Cat-a-lac
Block Coating Surface after Test



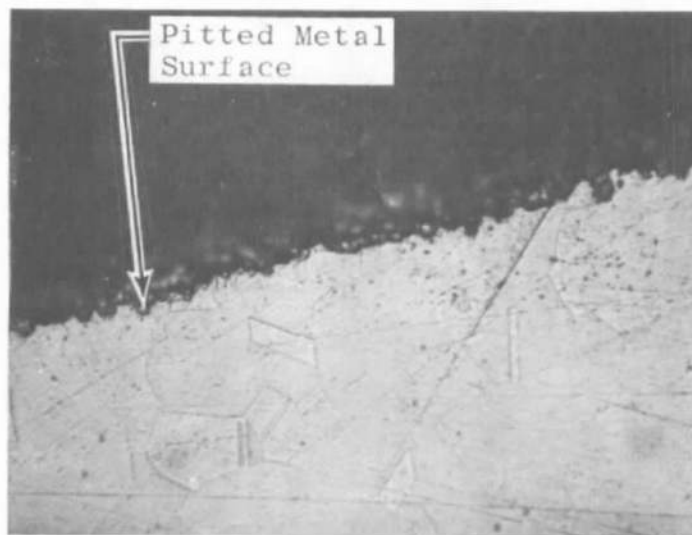
500X ETCHANT-OXALIC ELECTROLYTIC

Fig. 12 Micrograph of Cross Section of Cat-a-lac
Black Coated Stainless Steel

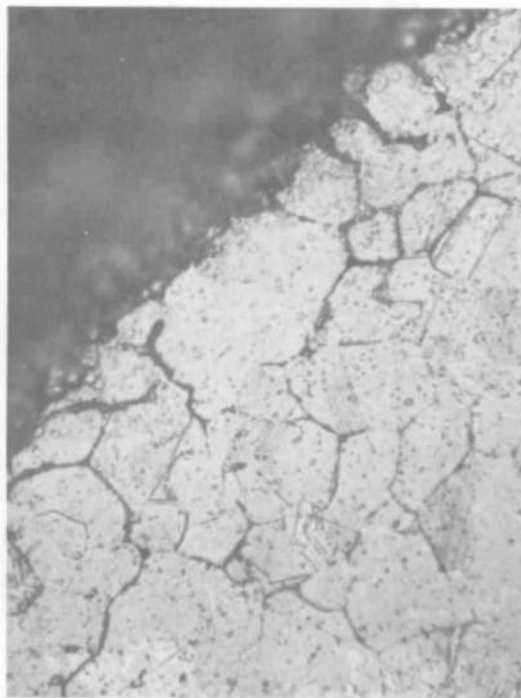


A E D C
2275-65

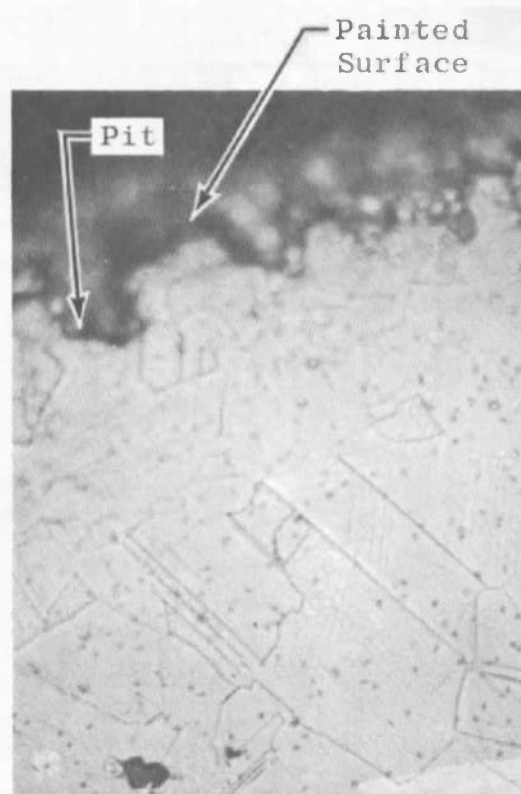
Fig. 13 Stainless Steel 304 Studs Welded to Steel
Cryoliner for Corrosion Tests



500X ETCHANT-OXALIC ELECTROLYTIC
Fig. 14 Micrograph of Cross Section of Stainless
Steel 304 Welded with 308 Rod

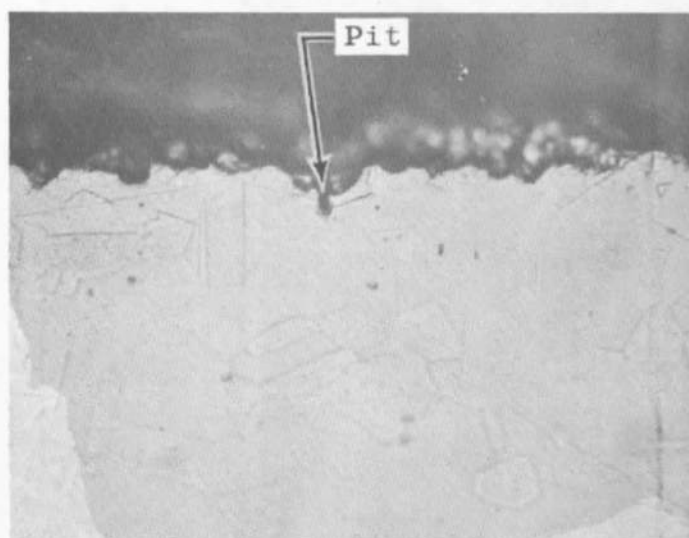


500X ETCHANT-OXALIC ELECTROLYTIC
Fig. 15 Micrograph of Cross Section of Weld
Sensitized Areas on Painted Stainless
Steel 304



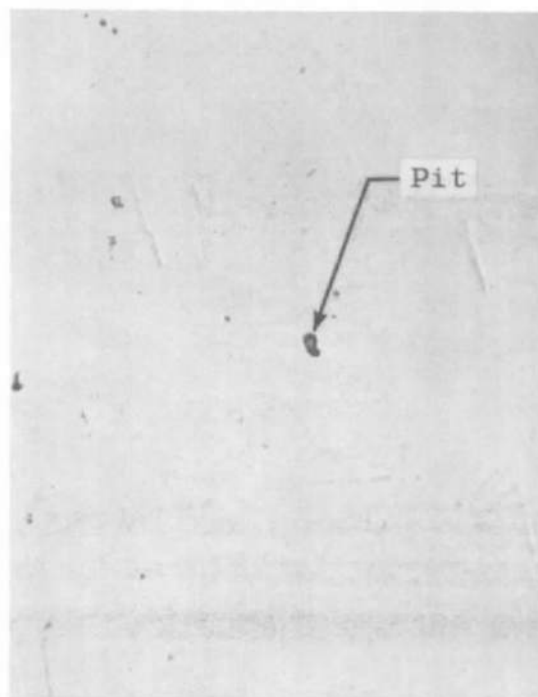
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Fig. 16 Micrograph of Cross Section of Cat-a-lac
Black Coated Stainless Steel 304 Welded
with Stainless Steel 304 Rod



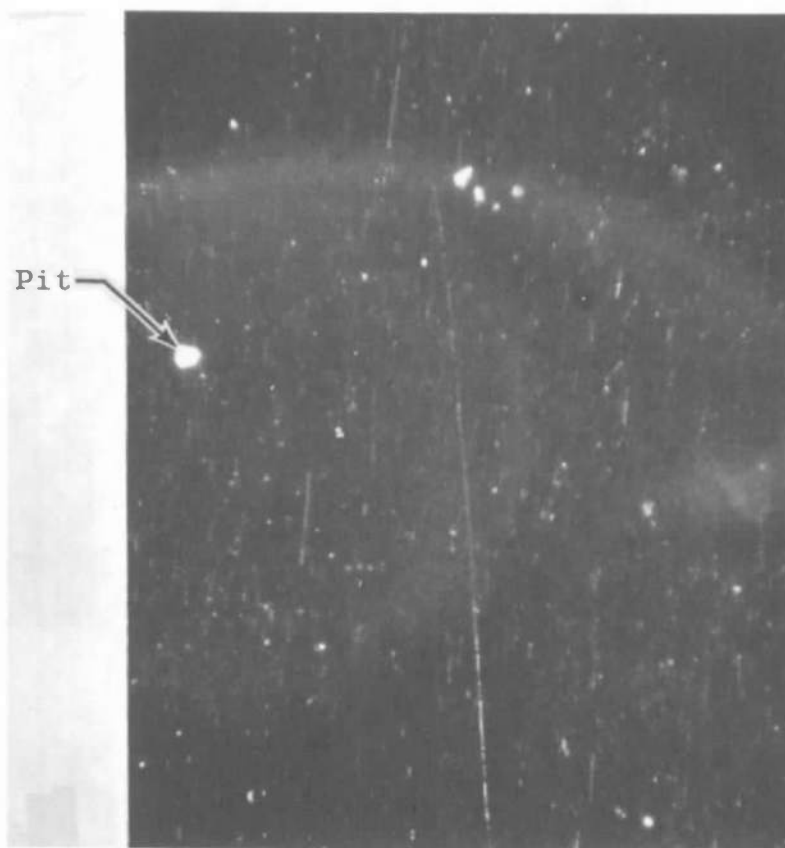
500X ETCHANT-OXALIC ELECTROLYTIC

Fig. 17 Micrograph of Cross Section of Cat-a-lac
Black Coated Stainless Steel 304 Welded
with Stainless Steel 308 Rod



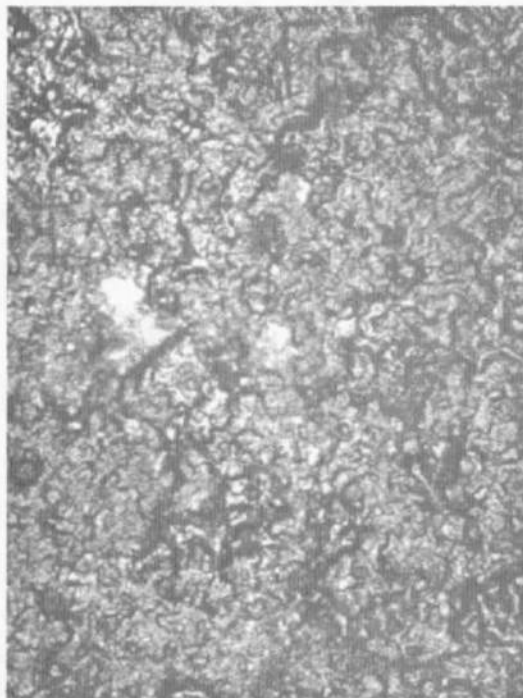
100X

Fig. 18 Micrograph of Pitted Surface of Heat-Treated
Stainless Steel 304-L



100X

Fig. 19 Micrograph of Pitted Surface of Heat-Treated
Stainless Steel 304-L



100X

**Fig. 20 Micrograph Showing Degraded Cat-a-loc
Black Coating and Pitted Stainless
Steel 304-L beneath the Coating**

TABLE I
SUMMARY OF CORROSION EFFECTS AND CONDITIONS WITH STAINLESS STEELS,
COATED AND UNCOATED, EXPOSED TO NITROGEN TETROXIDE

Sample	Nitrogen Tetroxide Exposure Conditions, torr/cycles	Time with Temperature > -150°F* (172°K), hr	Time with Temperature < -150°F* (172°K), hr	Observed Effects
Stainless steel 304 welded with 308 rod	3.9/5	8	206	General attack, intergranular corrosion in weld area, pitting, corrosion products
Cat-a-lac black coated stainless steel 304	3.9/5	8	206	Corrosion products on surface, no corrosion beneath coating
Stainless steel 304 welded with 304 and 308 rods	4.1/20	55	665	General pitting corrosion
Cat-a-lac black coated stainless steel 304 welded with 304 and 308 rods	4.1/20	55	665	Intergranular corrosion in weld areas, general pitting attack, some pitting of the coating
Stainless steel 304-L heat treated at 1075°F for 0.5 hr and polished	4.0/7	448	414	Surface pitting
Cat-a-lac black coated stainless steel 304-L heat treated at 1075°F for 0.5 hr and polished	4.0/7	448	414	Cracking and blistering of coating, microscopically detectable pitting of metal

*This temperature corresponds to the point at which a significant pressure rise occurs in the chamber, thus its use as a reference point

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13 ABSTRACT Corrosion of cryopanel metals in space simulation chambers caused by contamination by fuels, oxidizers, or exhaust gases arising from propulsion systems testing may be a serious problem. Since data taken under operational conditions is needed, a preliminary study using nitrogen tetroxide and 300-series stainless steel was initiated. The temperature was cycled between ambient conditions and 77°K, and the pressure between 4 and 10 ⁻⁵ torr of oxidizer. A black epoxy film covered some of the samples. Welded stainless steel 304 sustained general corrosion with some pitting, and intergranular corrosion was detected in heat-sensitized weld areas. Epoxy coated stainless steel 304 samples demonstrated no apparent damage in one series of short tests, but pit formation in the coating, pitting beneath the coating, and intergranular corrosion in weld areas was detected in a longer test. Heat-treated and polished stainless steel 304-L pitted to an indeterminate depth. An epoxy coated sample of similar material suffered microscopic cracking and blistering of the coating and surface pitting beneath.			

14	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	<p>corrosion contamination cryopanel space chambers nitrogen tetroxide stainless steel pitting</p> <p>2. Space chambers -- 3. " " 4. Steel -- Corrosion 5. Nitrogen tetroxide -- Pitting</p>						

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